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Number of claims of the invention: 5

Verification: not requested Number of pages (11)

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(54) Name of the invention: Manufacture of polymer interference films (Manufacture of diffraction lattices)

(21) Filed Number: Hei-Sei 4-170836

(22) Filed date: Hei-Sei 1 (1992) 6/29

Patent Assignee: Dainippon Printing Co.

# JP 6-11607

*[ Note : Names, addresses, Company names and brand names are translated in the most common manner. Japanese Language does not have singular or plural words unless otherwise specified with numeral prefix or general form of plurality suffix. Translator's note.]*

(54) [Name of the invention]

**Manufacture of polymer interference films (manufacture of diffraction lattice)**

**(57) [Summary]**

**[Goal]**

To manufacture a diffraction lattice where a diffraction is possible over a wide range of wavelengths, by the fact that two types and more polymer layers, that have different refraction indices, are laminated as in one part the thickness of the space between them is varied.

**[Structure]**

It is manufactured as a layer that is formed from 2 or more polymers with different refraction indices so that the refraction indices are repeated in the order :relatively high - low. And the laminated film is obtained as the high refraction index polymer layers 1, 3, 5 and the low refractive index polymer layers 2,4 6, are coated in that order. Because of the fact that it is a laminated layer film where the thickness of the space between the layers, is varied, it is possible to have a range of the refracted wavelengths, for example, in the range of 800 nm ~ 2000 nm. In this case, it becomes a good heat rays reflecting layer, which is permeable to the visible light, but reflects the heat rays. Besides that, there are also other applications like color filters where a light with specific wavelength from the visible light region, is reflected, film cutting off the ultra-violet rays etc..

**[Range of the claims of the invention]**

[Claim 1]

Diffraction lattice manufacturing method, characterized by the fact that, it is manufactured as a layer that is formed from 2 or more polymers with different refraction indices so that the refraction indices are repeated in the

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order :relatively high - low. And the laminated film is obtained as the high refraction index polymer layers and the low refractive index polymer layers are coated in that order and laminated.

[Claim 2]

Manufacturing method for the preparation of a diffraction lattice, according to the above described Claim 1, characterized by the fact that it is manufactured as the polymer layer thickness is different from at least one part of the space between the layers, and it is possible to have a diffraction over a wide range of wavelengths.

[Claim 3]

Manufacturing method for the preparation of a diffraction lattice, according to the above described Claim 1, and Claim 2, characterized by the fact that the polymer layers are coated by using a dissolved polymer solution, where it is dissolved in a solvent that can be eliminated by heating and that does not dissolve the polymer layers.

[Claim 4]

Manufacturing method for the preparation of a diffraction lattice, according to the above described Claim 1, and Claim 2, characterized by the fact that the polymer layers are coated by coating of an ionized radiation beam curable solution, capable of forming a polymer layer by irradiation with an ionized radiation beam.

[Claim 5]

Manufacturing method for the preparation of a diffraction lattice according to the above described Claims from 1 to 4, characterized by the fact that as the coating method spin-coating is used.

**[Detailed description of the invention]**

[0001]

**[Technological sphere of application]**

The present invention is an invention about the manufacturing method of a diffraction lattice. And especially, it is an invention about the manufacturing method of a diffraction lattice, like a thermal radiation reflecting layer, that diffracts over a wide range of wavelengths.

[0002]

[Previous technology]

As diffraction lattices, according to the previous technology, the Bragg diffraction lattices are well known where in layers of photo-polymers, bichromate - gelatine, silver salts etc., the light interference image is recorded and formed.

However, regarding these lattices, in all cases, the range of the diffraction wavelengths, is narrow, and constructions that are capable of diffracting over a wide range of wavelengths, have not been obtained.

[0003]

In order to use such Bragg diffraction lattice as a thermal rays reflecting layer etc., it is necessary that the diffraction wavelength is accomplished within a range of over several hundred nm.

[0004]

[Problems solved by the present invention]

The present invention, is an invention that is based on such considerations of the circumstances, and its goal is to suggest a manufacturing method for the preparation of a Bragg diffraction lattice where a diffraction is possible over a wide range of wavelengths. This is accomplished by the fact that two types and more polymer layers, are laminated as in one part the thickness of the space between the layers is varied.

[0005]

[Measures in order to solve the problems]

According to the manufacturing method of the present invention, in order to solve the above described problems, it is a manufacturing method for the preparation of a polymer layer where polymer layers with different refractive indices are laminated and where at least in one part the thickness of the space between the layers is different. And in this method, as the coating methods, spin-coating method is used and the layer thickness control is accomplished by the change in the viscosity of the coating solution and the number of revolutions per minute (rpm) during the spin coating process. Because of that, the diffraction coefficient and the diffraction wavelength, can be set freely by varying the polymer layer thickness, the number of the laminated layers, the difference between the refraction coefficients. And it is a very simple, for the manufacturing of diffraction lattices with a wide range of applications.

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[0002]

[0006]

Usually, if the incident angle is denoted as $\theta$, and the refraction coefficient - as n, the lattice space pitch, d, and the diffraction wavelength $\lambda$, are according to the following

$$2nd \sin \theta = m \quad ( m = 1,2, 3.....)$$

Consequently,if the structure of the diffraction lattice is formed as a layer with a high refraction coefficient and a layer with a low refraction coefficient are laminated opposite to each other, at this time, by manufacturing several types of layers that have different lattice space pitch d, it is possible to realize a diffraction of different wavelength light. And it is possible to widen the diffraction wavelength range of one diffraction lattice.

[0007]

If we are to explain an example in more detail, in the case when the average refractive coefficient is 1.5, as it is shown in the sectional view diagram in Figure 1, for example, 5 combinations of a 0.13 micron thick high refraction coefficient polymer layer 1 (nd = 1.59) and the same thickness, low refraction coefficient polymer layer 2 (nd = 1.41) are laminated ; and after that 5 combinations of 0.14 micron thick high refraction coefficient polymer layer 3 (nd= 1.59) and the same thickness low refraction coefficient polymer layer 4 (nd = 1.41) are laminated; and the layer lamination is repeated as the thickness is progressively increased, and 5 combinations of 0.67 micron thick high refraction coefficient polymer layer 5 (nd= 1.59) and the same thickness low refraction coefficient polymer layer 6 (nd = 1.41) are laminated and the diffraction lattice 10, is manufactured. The film thickness of this film 10, became 70 microns, as calculated according to the following calculations:

[0008]

$$0.13 \times 2 \times 5 + 0.14 \times 2 \times 5 + .... + 0.67 \times 2 \times 5 = 70 \text{ microns}$$

By using this diffraction lattice 10, as it is shown in Figure 2, by the first thickness layer combination, 1 and 2, light with a wavelength of 800 nm, is diffracted, and by the combinations of the progressively increasing in thickness layers, a diffraction is accomplished over a wide range of 840 nm , ......., 2000 nm. Then, by varying the polymer layer thickness, the number of the laminated layers, and the difference in the refraction coefficient, it is possible to set freely the diffraction wavelength range and the diffraction coefficient.

[0009]

As methods in order to obtain such a layered structure, different coating processes can be considered, like, roll coating, gravure coating, die coating, spray coating, blade coating, spin coating etc., and each of this coating processes can be appropriately used in the present invention. Among those, as an especially preferred coating method, there is the spin coating method where the layer thickness control is 0.01 micron units, and also it is a very strict control.

[0010]

Also, regarding the polymers that form the polymer layers according to the present invention,it is preferred that they are coated by the spin coating method by using polymer solutions or ionization radiation beam curable type material solution.

[0011]

First, here below the case when it is coated by using a polymer solution, will be explained. In the case when it is coated by using a polymer solution, it is necessary that each of the described here below conditions is satisfied.

(1) Regarding the polymer, it is dissolved in a solvent that after the spin coating can be heated and dried off.

(2) The refraction coefficients of the two polymers are mutually different.

(3) the solvent that dissolves one of the polymers, does not dissolve the layer of the other polymer.

As polymer compositions that satisfy the above described conditions, those can be determined as the polymer handbook etc., is used, and the refraction coefficients, solvents and nonsolvents are studied.

[0012]

As the polymers that can be used in the manufacturing method according to the present invention, for example,

| | |
|---|---|
| polyvinylidenefluoride | 1.42 |
| polydimethylsilylene (polydimethylsiloxane) | 1.43 |
| polytrifluoroethylmethacrylate | 1.437 |
| polyoxypropylene | 1.4495 |
| polyvinylisobutylether | 1.4507 |
| polyvinylethylether | 1.4540 |
| polyoxyethylene | 1.4563 |

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[0009]

| | |
|---|---|
| polyvinylbutylether | 1.4563 |
| polyvinylpentylether | 1.4581 |
| polyvinylhexylether | 1.4591 |
| poly(4-methy-1-pentene) | 1.459 ~ 1.465 |
| cellulose acetate butylate | 1.46 ~ 1.49 |
| poly(4-fluoro-2-trifluoromethylstyrene) | 1.46 |
| polyvinyloctylether | 1.4613 |
| poly(vinyl 2-ethylhexylether) | 1.4626 |
| polyvinyldecylether | 1.4628 |
| poly(2-methoxyethylacrylate) | 1.463 |
| polybutylacrylate | 1.4631 |
| polybutylacrylate | 1.466 |
| poly(t-butylmethacrylate) | 1.4638 |
| polyvinyldodecylether | 1.4640 |
| poly (3-ethoxypropylacrylate) | 1.465 |
| polyoxycarbonyltetramethylene | 1.465 |
| polyvinylpropionate | 1.4665 |
| polyvinylacetate | 1.4665 |
| polyvinylmethylether | 1.467 |
| polyethylacrylate | 1.4685 |
| ethylene-vinyl acetate copolymer (80 % ~ 20 % vinylacetate) | 1.47 ~ 1.50 |
| cellulose propionate | 1.47 ~ 1.49 |
| cellulose acetate propionate | 1.47 |
| benzylcellulose | 1.47 ~ 1.58 |
| phenol formaldehyde resin | 1.47 ~ 1.70 |
| cellulose triacetate | 1.47 ~ 1.48 |
| polyvinylmethylether (isotactic) | 1.4700 |
| poly (3-methoxypropylacrylate) | 1.471 |
| poly(2-ethoxyethylacrylate) | 1.471 |
| polymethylacrylate | 1.472 ~ 1.480 |
| polyiospropylemethacrylate | 1.4728 |
| poly (1-decene) | 1.4730 |
| polypropylene (atactic, density 0.8575 g/cm3) | 1.4735 |
| poly(vinyl sec-butylether) (isotactic) | 1.4740 |
| polydodecylmethacrylate | 1.4740 |
| polyoxyethyleneoxysuccinoyl (polyethylenesuccinate) | 1.4744 |
| polytetradecylmethacrylate | 1.4746 |
| ethylene - propylene copolymer material (EPR rubber) | 1.4748 ~ 1.48 |
| polyhexadecylmethacrylate | 1.4750 |
| polyvinylformate | 1.4757 |
| poly(2-fluoroethylmethacrylate) | 1.4768 |
| polyisobutylmethacrylate | 1.477 |
| ethyl cellulose | 1.479 |
| polyvinylacetal | 1.48 ~ 1.50 |

| | |
|---|---|
| cellulose acetate | 1.48 ~ 1.50 |
| cellulose tripropionate | 1.48 ~ 1.49 |
| polyoxymethylene | 1.48 |
| polyvinylbutyral | 1.48 ~ 1.49 |
| poly (n-hexylmethacrylate) | 1.4813 |
| poly (n-butylmethacrylate) | 1.483 |
| polyethylidenedimethacrylate | 1.4831 |
| poly (2-ethoxyethylmethacrylate) | 1.4833 |
| polyoxyethyleneoxymaleoyl (polyethylene maleate) | 1.4840 |
| poly (n-propylmethacrylate) | 1.484 |
| poly (3, 3, 5-trimethylcyclohexylmethacrylate) | 1.485 |
| polyethylmethacrylate | 1.485 |
| poly(2-nitro-2-methylpropylmethacrylate) | 1.4868 |
| polytriethylcarbinylmethacrylate | 1.4889 |
| poly (1,1'-diethylpropylmethacrylate) | 1.4889 |
| polymethylmethacrylate | 1.4893 |
| | 1.490 |
| poly (2-decyl-1,3-butadiene) | 1.4899 |
| polyvinyl alcohol | 1.49 ~ 1.53 |
| polyethylglycolate methacrylate | 1.4903 |
| poly (3-methylcyclohexylmethacrylate) | 1.4947 |
| poly(cycloehexyl alpha-ethoxyacrylate) | 1.4969 |
| methylcellulose (low density) | 1.497 |
| poly(4-methylcyclohexylmethacrylate) | 1.4975 |
| polydecamethyleneglycoldimethacrylate | 1.4990 |
| polyurethane | 1.5 ~ 1.6 |
| poly (1,2-butadiene ) | 1.5000 |
| polyvinylformal | 1.50 |
| poly (2-bromo-4-trifluoromethylstyrene) | 1.5 |
| cellulose nitrate | 1.50 ~ 1.514 |
| poly (sec-butyl alpha-chloroacrylate) | 1.500 |
| poly (2-heptyl-1,3-butadiene) | 1.5000 |
| poly (ethyl-alpha-chloroacrylate) | 1.502 |
| poly (2-isopropyl- 1,3-butadiene) | 1.5028 |
| poly (2-methylcyclohexylmethacrylate) | 1.5028 |
| polypropylene(density 0.9075 g/cm3) | 1.5030 |
| polyisobutene | 1.505 ~ 1.51 |
| polyborunylmethacrylate | 1.5059 |
| poly (2-t-butyl-1,3-butadiene) | 1.5060 |
| polyethyleneglycoldimethacrylate | 1.5063 |
| polycyclohexylmethacrylate | 1.5066 |
| poly (cyclohexanediol -1,4-dimethacrylate) | 1.5067 |
| butyl rubber (not vulcanized) | 1.508 |
| polytetrahydrofurfurylmethacrylate) | 1.5096 |
| gudaperca (beta) | 1.509 |

| | |
|---|---|
| cellulose acetate | 1.48 ~ 1.50 |
| cellulose tripropionate | 1.48 ~ 1.49 |
| polyoxymethylene | 1.48 |
| polyvinylbutyral | 1.48 ~ 1.49 |
| poly (n-hexylmethacrylate) | 1.4813 |
| poly (n-butylmethacrylate) | 1.483 |
| polyethylidenedimethacrylate | 1.4831 |
| poly (2-ethoxyethylmethacrylate) | 1.4833 |
| polyoxyethyleneoxymaleoyl (polyethylene maleate) | 1.4840 |
| poly (n-propylmethacrylate) | 1.484 |
| poly (3, 3, 5-trimethylcyclohexylmethacrylate) | 1.485 |
| polyethylmethacrylate | 1.485 |
| poly(2-nitro-2-methylpropylmethacrylate) | 1.4868 |
| polytriethylcarbinylmethacrylate | 1.4889 |
| poly (1,1'-diethylpropylmethacrylate) | 1.4889 |
| polymethylmethacrylate | 1.4893 |
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| poly (1,2-butadiene ) | 1.5000 |
| polyvinylformal | 1.50 |
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| poly (2-heptyl-1,3-butadiene) | 1.5000 |
| poly (ethyl-alpha-chloroacrylate) | 1.502 |
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| poly(4-fluoro-2-trifluoromethylstyrene) | 1.46 |
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| polyvinyldodecylether | 1.4640 |
| poly (3-ethoxypropylacrylate) | 1.465 |
| polyoxycarbonyltetramethylene | 1.465 |
| polyvinylpropionate | 1.4665 |
| polyvinylacetate | 1.4665 |
| polyvinylmethylether | 1.467 |
| polyethylacrylate | 1.4685 |
| ethylene-vinyl acetate copolymer (80 % ~ 20 % vinylacetate) | 1.47 ~ 1.50 |
| cellulose propionate | 1.47 ~ 1.49 |
| cellulose acetate propionate | 1.47 |
| benzylcellulose | 1.47 ~ 1.58 |
| phenol formaldehyde resin | 1.47 ~ 1.70 |
| cellulose triacetate | 1.47 ~ 1.48 |
| polyvinylmethylether (isotactic) | 1.4700 |
| poly (3-methoxypropylacrylate) | 1.471 |
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| poly(vinyl sec-butylether) (isotactic) | 1.4740 |
| polydodecylmethacrylate | 1.4740 |
| polyoxyethyleneoxysuccinoyl (polyethylenesuccinate) | 1.4744 |
| polytetradecylmethacrylate | 1.4746 |
| ethylene - propylene copolymer material (EPR rubber) | 1.4748 ~ 1.48 |
| polyhexadecylmethacrylate | 1.4750 |
| polyvinylformate | 1.4757 |
| poly(2-fluoroethylmethacrylate) | 1.4768 |
| polyisobutylmethacrylate | 1.477 |
| ethyl cellulose | 1.479 |
| polyvinylacetal | 1.48 ~ 1.50 |

| | |
|---|---|
| polyethylene ionomer | 1.51 |
| polyoxyethylene (high molecular weight) | 1.51 ~ 1.54 |
| polyethylene (density 0.914 g/cm3) | 1.51 |
| (density 0.94 ~ 0.945 g/cm3) | 1.52 ~ 1.53 |
| (density 0.965 g/cm3) | 1.545 |
| poly (1-methylcyclohexylmethacrylate) | 1.5111 |
| poly (2-hydroxyethylmethacrylate) | 1.5119 |
| polyvinylchloroacetate | 1.512 |
| polybutene (isotactic) | 1.5125 |
| polyvinylmethacrylate | 1.5129 |
| poly (N-butyl-methacrylamide) | 1.5135 |
| gutaperca (alpha) | 1.514 |
| terpenic resin | 1.515 |
| poly (1,3-butadiene) | 1.5154 |
| shelac | 1.51 ~ 1.53 |
| poly (methyl alpha-chloroacrylate) | 1.517 |
| poly (2-chloroethylmethacrylate) | 1.517 |
| poly (2-diethylaminoethylmethacrylate | 1.5174 |
| poly (2-chlorocyclohexylmethacrylate) | 1.5179 |
| poly (1,3-butadiene) (35 % cis; 56 % trans; 7 %, 2- contet) | 1.5180 |
| natural rubber | 1.519 ~ 1.52 |
| polyallylmethacrylate | 1.5196 |
| polyvinyl chloride + 40 % octylphthalate | 1.52 |
| polyacrylonitrile | 1.52 |
| | 1.5187 |
| polymethacrylonitrile | 1.52 |
| poly (1, 3-butadiene ) (sic type rich) | 1.52 |
| butadiene - acrylonitrile copolymer material | 1.52 |
| polymethylisopropenyl ketone | 1.5200 |
| polyisoprene | 1.521 |
| polyester resin rigid ( approximately 50 % styrene) | 1.523 ~ 1.54 |
| poly (N- (2-methoxyethyl)methacrylamide) | 1.5246 |
| poly (2,3-dimethylbutadiene) (methyl rubber) | 1.525 |
| vinyl chloride - vinyl acetate copolymer material (95/5 ~ 90/10) | 1.525 ~ 1.535 |
| polyacrylic azide | 1.527 |
| poly (1,3-dichloropropylmethacrylate) | 1.5270 |
| poly (2-chloro-1- (chloromethyl) ethylmethacrylate) | 1.5270 |
| polyacroleine | 1.529 |
| poly (1-vinyl -2- pyrolidone) | 1.53 |
| hydrochloric acid reacted rubber | 1.53 ~ 1.55 |
| Nylon 6; Nylon 6,6; Nylon 6, 10 (synthetic type material) (Nylon 6-fiber; 1.515 in the transverse direction; 1.565 in the fiber direction) | 1.53 |
| butadiene - styrene copolymer material (approximately 30 % styrene) block copolymer | 1.53 |
| poly (cyclohexyl alpha-chloroacrylate) | 1.532 |

| | |
|---|---|
| poly (2-chloroethyl alpha-chloroacrylate) | 1.533 |
| butadiene-styrene copolymer material (approximately 75/25) | 1.535 |
| poly (2-aminoethylmethacrylate) | 1.537 |
| polyfurfurylmethacrylate | 1.5381 |
| protein | 1.539 ~ 1.541 |
| polybutylmercaptylmethacrylate | 1.5390 |
| poly (1-phenyl-n-amylmethacrylate) | 1.5396 |
| poly (N-methyl-methacrylamide) | 1.5398 |
| cellulose | 1.54 |
| polyvinylchloride | 1.54 ~ 1.55 |
| urea- formaldehyde resin | 1.54 ~ 1.56 |
| poly (sec-butyl alpha-bromoacrylate) | 1.542 |
| poly (cyclohexyl alpha-bromoacrylate) | 1.542 |
| poly (2-bromoethylmethacrylate) | 1.5426 |
| polydihydroabietic acid | 1.544 |
| polyabietic acid | 1.546 |
| polyethylmercaptylmethacrylate | 1.547 |
| poly (N-allylmethacrylamide) | 1.5476 |
| poly (1-phenylethylmethacrylate) | 1.5487 |
| polyvinylfuran | 1.55 |
| poly (2-vinyltetrahydrofuran) | 1.55 |
| poly (vinyl chloride) + 40 % tricrezyl phosphate | 1.55 |
| epoxy resin | 1.55 ~ 1.60 |
| poly (p-methoxybenzylmethacrylate) | 1.552 |
| polyisopropylmethacrylate | 1.552 |
| poly (p-isopropylstyrene) | 1.554 |
| polychloroprene | 1.554 ~ 1.558 |
| poly (oxyethylene-alpha-benzoate- -methacrylate) | 1.555 |
| poly (p,p'-xylilenyldimethacrylate) | 1.5559 |
| poly (1-phenylallylmethacrylate) | 1.5573 |
| poly(p-cyclohexylphenylmethacrylate) | 1.5575 |
| poly (2-phenylethylmethacrylate) | 1.5592 |
| poly (oxycarbonyloxy -1,4-phenylene-1-propyl-butylidene 1,4-phenylene) | 1.5602 |
| poly ( 1-(o-chlorophenyl)ethylmethacrylate) | 1.5624 |
| styrene - anhydrous maleic acid copolymer material | 1.564 |
| poly (1-phenylcyclohexylmethacrylate) | 1.5645 |
| poly (oxycarbonyloxy-1,4-phenylene 1,3-dimethyl- butylidene - 1,4-phenylene ) | 1.5671 |
| poly (methyl alpha - bromoacrylate) | 1.5672 |
| polybenzylmethacrylate | 1.5680 |
| poly (2-( phenylsulfonyl)ethylmethacrylate) | 1.5682 |
| poly(m-crezylmethacrylate) | 1.5683 |
| styrene - acrylonitrile copolymer material (approximately 75/25) | 1.57 |
| poly (oxycarbonyloxy-1,4-phenyleneisobutylidene -1,4-phenylene) | 1.5702 |
| poly (o-methoxyphenylmethacrylate) | 1.5705 |

| | |
|---|---|
| poly (2-chloroethyl alpha-chloroacrylate) | 1.533 |
| butadiene-styrene copolymer material (approximately 75/25) | 1.535 |
| poly (2-aminoethylmethacrylate) | 1.537 |
| polyfurfurylmethacrylate | 1.5381 |
| protein | 1.539 ~ 1.541 |
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| poly (1-phenyl-n-amylmethacrylate) | 1.5396 |
| poly (N-methyl-methacrylamide) | 1.5398 |
| cellulose | 1.54 |
| polyvinylchloride | 1.54 ~ 1.55 |
| urea- formaldehyde resin | 1.54 ~ 1.56 |
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| poly (cyclohexyl alpha-bromoacrylate) | 1.542 |
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| poly (vinyl chloride) + 40 % tricrezyl phosphate | 1.55 |
| epoxy resin | 1.55 ~ 1.60 |
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| polyisopropylmethacrylate | 1.552 |
| poly (p-isopropylstyrene) | 1.554 |
| polychloroprene | 1.554 ~ 1.558 |
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| poly (p,p'-xylilenyldimethacrylate) | 1.5559 |
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| poly (o-methoxyphenylmethacrylate) | 1.5705 |

| | |
|---|---|
| polyethylene ionomer | 1.51 |
| polyoxyethylene (high molecular weight) | 1.51 ~ 1.54 |
| polyethylene (density 0.914 g/cm3) | 1.51 |
| (density 0.94 ~ 0.945 g/cm3) | 1.52 ~ 1.53 |
| (density 0.965 g/cm3) | 1.545 |
| poly (1-methylcyclohexylmethacrylate) | 1.5111 |
| poly (2-hydroxyethylmethacrylate) | 1.5119 |
| polyvinylchloroacetate | 1.512 |
| polybutene (isotactic) | 1.5125 |
| polyvinylmethacrylate | 1.5129 |
| poly (N-butyl-methacrylamide) | 1.5135 |
| gutaperca (alpha) | 1.514 |
| terpenic resin | 1.515 |
| poly (1,3-butadiene) | 1.5154 |
| shelac | 1.51 ~ 1.53 |
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| hydrochloric acid reacted rubber | 1.53 ~ 1.55 |
| Nylon 6; Nylon 6,6; Nylon 6, 10 (synthetic type material) (Nylon 6-fiber; 1.515 in the transverse direction; 1.565 in the fiber direction) | 1.53 |
| butadiene - styrene copolymer material (approximately 30 % styrene) block copolymer | 1.53 |
| poly (cyclohexyl alpha-chloroacrylate) | 1.532 |

| | |
|---|---|
| polyphenylmethacrylate | 1.5706 |
| poly (o-crezylmethacrylate) | 1.5707 |
| polydiallylphtalate | 1.572 |
| poly (2,3-dibromopropylmethacrylate) | 1.5739 |
| poly (oxycarbonyloxy - 1,4-phenylene -1-methyl-butylidene-1,4-phenylene) | 1.5745 |
| poly (oxy-2,6-dimethylphenylene) | 1.575 |
| polyoxyethyleneoxyterephtaloyl (amorphous) (polyethylene terephtalate) (crystalline fiber: 1.51 in the transverse direction 1.64 in the directon of the fiber) | 1.5750 |
| polyvinyl benzoate | 1.5775 |
| poly(oxycarbonyloxy -1,4-phenylene butylidene-1,4-phenylene) | 1.5792 |
| poly (1,2-diphenyl ethylmethacrylate) | 1.5816 |
| poly (o-chlorobenzylmethacrylate) | 1.5823 |
| poly(oxycarbonyloxy - 1,4-phenylene -sec-butylidene-1,4-phenylene ) | 1.5827 |
| polyoxypentaerithritoxyphtaloyl) | 1.584 |
| poly (m-nitrobenzylmethacrylate) | 1.5845 |
| poly(oxycarbonyloxy -1,4- phenyleneisopropylidene-1,4-phenylene) | 1.5850 |
| poly (N-(2-phenylethyl) methacrylamide) | 1.5857 |
| poly(4-methoxy--2- methylstyrene) | 1.5868 |
| poly (o-methylstyrene) | 1.5874 |
| polystyrene | 1.59 ~ 1.592 |
| poly(oxycarbonyloxy-1,4-phenylenecyclohexylidene-1,4-phenylene) | 1.5900 |
| poly (o-methoxystyrene) | 1.5932 |
| polydiphenylmethylmethacrylate | 1.5933 |
| poly(oxycarbonyloxy-1,4-phenyleneethylidene-1,4-phenylene) | 1.5937 |
| poly (p-bromophenylmethacrylate) | 1.5964 |
| poly (N-benzylmethacrylamide) | 1.5965 |
| poly (p-methoxystyrene) | 1.5967 |
| hardened rubber ( 32 % S) | 1.6 |
| polyvinylidene chloride | 1.60 ~ 1.63 |
| polysulfide ("Thiokol") | 1.6 ~ 1.7 |
| poly (o-chlorodiphenylmethylmethacrylate) | 1.6040 |
| poly (oxycarbonyloxy-1,4- (2,6-dichloro) phenylene -isopropylidene - 1,4-(2,6-dichloro) phenylene) | 1.6056 |
| poly(oxycarbonyloxybis (1,4-(3,5-dichloropehnylene))) | 1.6056 |
| polypentachlorophenylmethacrylate | 1.608 |
| poly (o-chlorostyrene) | 1.6098 |
| poly(phenyl alpha- brmoacrylate) | 1.612 |
| poly(p-divinylbenzene) | 1.6150 |

| | |
|---|---|
| poly (N-vinylphtalimide) | 1.6200 |
| poly(2,6-dichlorostyrene) | 1.6248 |
| poly(beta-napthylmethacrylate) | 1.6298 |
| poly(alpha-naphthylcarbinylmethacrylate) | 1.63 |
| polysulfon | 1.633 |
| poly (2-vinylthiophen) | 1.6376 |
| poly (alpha-naphtylmethacrylate) | 1.6410 |
| poly (oxycarbonyloxy-1,4-phenylenediphenyl-methylene - 14,-phenylene) | 1.6539 |
| polyvinylphenylsulfide | 1.6568 |
| butylphenolformaldehyde resin | 1.66 |
| urea - thiourea- formaldehyde resin | 1.660 |
| polyvinylnaphthalene | 1.6818 |
| polyvinylcarbazol | 1.683 |
| naphthalene - formaldehyde resin | 1.696 |
| phenol -formaldehyde resin | 1.70 |
| polypentabromophenylmethacrylate | 1.71 |

etc., can be used. Moreover, regarding the above described compounds, the d line refraction coefficient (nd) is also shown.

[0013]

Also, as representative solvents, methanol, ethanol, n-propanol, isopropanol, amyl alcohol, acetone, methylethylketone, methylisobutylketone, ethylenechloride, chloroform, benzene, toluene, xylene, hexene, heptane, cyclohexane, etc., relatively low boiling point organic solvents and water can be used.

[0014]

The case when it is coated as the ionization radiation beam curable type material solution, is described here below. As the ionization radiation beam curable type material, there are the ionization radiation beam curable type resins and ultra-violet light curable type resins. And regarding these ionization radiation beam curable type resins and ultra-violet light curable type resins, except for the fact that in the latter, a polymerization initiation agent and a sensitivity increasing agent, are contained, the other components are the same. And usually, as a component of the cover layer forming material, there is a material whose main component is a polymer, oligomer, or monomer that contains in its structure a radical that is active in the radical polymerization reaction. And it is preferred that the viscosity of this material is less than 2000 cps. As such a polymer or oligomer material, materials that re easily available as commercial products, like urethane acrylate or polyester acrylate, can be appropriately used according to the present invention. As the monomer material, the commercially available acrylic acid or methacrylic acid derivative materials etc., ionization radiation beam curable type

| | |
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| poly(oxycarbonyloxy-1,4-phenylenecyclohexylidene-1,4-phenylene) | 1.5900 |
| poly (o-methoxystyrene) | 1.5932 |
| polydiphenylmethylmethacrylate | 1.5933 |
| poly(oxycarbonyloxy-1,4-phenyleneethylidene-1,4-phenylene) | 1.5937 |
| poly (p-bromophenylmethacrylate) | 1.5964 |
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| poly (o-chlorostyrene) | 1.6098 |
| poly(phenyl alpha- brmoacrylate) | 1.612 |
| poly(p-divinylbenzene) | 1.6150 |

monomers, can be appropriately used according to the present invention. In order to make the above described curable resins ultra-violet light curable resins, in that, it is possible to use and mix as a light polymerization agent, acetophenone type, benzophenone, mihira- benzoylbenzoate, alpha-amineoximeester, tetramethylthiorame monosulfide, thioxantane etc., types, and as an agent increasing the light sensitivity,, it is possible to use and mix n-butylamine, triethylamine, tri-n-butylphosphine etc..

[0015]

In this case, by using spin coating, the above described material is coated at the desired thickness, and after that it is irradiated by using an ionized irradiation beam method. And it is possible to use the previous technology in the state as it is, for example, in the case of the electron beam radiation, the Kokuroft Walton type, Bandegraf type, resonance pressure change type, insulated core pressure change type, direct beam type, Dynamitron type, high frequency type, etc., it can be irradiated from different types of electron beam acceleration devices. And it is an electron beam that has an energy in the range of 50 ~ 1,000 KeV, and preferably, it is in the range of 100 ~ 300 KeV. And by using this beam in the range of 0.1 ~ 100 Mrad, and preferably, in the range of 1 ~ 10 Mrad, are irradiated and by that it is possible to cure the material. And also, in the case of the ultra-violet irradiation, by using the ultra-violet light beam that is generated from a light source like an ultra-high pressure mercury lamp, high pressure mercury lamp, carbon arc, xenone arc, metal hallide lamp etc., a radiation in the range of 0.1 ~ 10,000 mJ/cm2, preferably, in the range of 10 ~ 1,000 mJ/cm2, is generated and by that it is possible to accomplish the cure.

[0016]

Usually, in the spin coating method, the thickness, h, of the coating layer, is represented by

$$h = K\mu^{0.36}\omega^{-0.50}(E\mathcal{J}/C_p)^{0.60}$$

Here, K : constant, $\mu$ : viscosity of the coating material, $\omega$ : angular velocity of the spinner, E : relative evaporation rate, $\mathcal{J}$ : evaporation hidden heat, Cp : heat capacity.

[0017]

Consequently, regarding the conditions for coating a polymer layer with a desired thickness, in advance, the polymer solution is adjusted to the desired viscosity and it is coated a the desired number of rpms, and by that the relationship between the layer thickness and the rpms, is established. And it is possible to determined the desired coating thickness from that relationship.

[0018]

As it is clear from the above described explanation, the manufacturing method for the preparation of the diffraction lattice according to the present invention, is a manufacturing method characterized by the fact that layers formed from 2 and more polymer layers with different refraction coefficients are repeated so that the relatively high and the relatively low refraction indices are repeated, and the high refraction index polymer layer and the low refraction index polymer layer are coated in order and by that they are laminated.

[0019]

In this case, the fact that the polymer layer thickness is made so that at least in one part is is different from the layer space, is required so that a diffraction over a wide range of wavelengths can be conducted.

[0020]

Also, regarding the polymer layers, they are produced by coating a polymer solution where the polymer is dissolved in a solvent medium that can be eliminated by heating and drying and also that does not dissolve the polymer layers, or it is manufactured by coating an ionized radiation beam curable type solution, where the polymer layer can be formed by irradiation with an ionized radiation beam.

[0021]

In the case when the polymer solution is snapping etc., and by that it is difficult to accomplish a homogeneous coating, it is possible to solve this problem by using a surface treatment, like a corona treatment, ozone treatment etc..

[0022]

Moreover, it is preferred to use spin coating as the coating method.

[0023]

**[Effect]**

According to the present invention, it is a manufacturing method characterized by the fact that layers formed from 2 and more polymer layers with different refraction coefficients are repeated so that the relatively high and the relatively low refraction indices are repeated, and the high refraction

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**[Effect]**

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monomers, can be appropriately used according to the present invention. In order to make the above described curable resins ultra-violet light curable resins, in that, it is possible to use and mix as a light polymerization agent, acetophenone type, benzophenone, mihira- benzoylbenzoate, alpha-amineoximeester, tetramethylthiorame monosulfide, thioxantane etc., types, and as an agent increasing the light sensitivity,, it is possible to use and mix n-butylamine, triethylamine, tri-n-butylphosphine etc..

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Consequently, regarding the conditions for coating a polymer layer with a desired thickness, in advance, the polymer solution is adjusted to the desired viscosity and it is coated a the desired number of rpms, and by that the relationship between the layer thickness and the rpms, is established. And it is possible to determined the desired coating thickness from that relationship.

index polymer layer and the low refraction index polymer layer are coated in order and by that they are laminated. And because of that, a laminated layer is obtained where the spaces between the layers are different and by that it is possible to easily manufacture a diffraction lattice with a wide range of diffraction wavelengths.

[0024]

[Practical example]

Here below, a practical example of the manufacturing method for the preparation of a diffraction lattice, according to the present invention, will be explained.

Practical Example 1

As a high refraction coefficient polymer layer, polystyrene (PSt, nd=1.592) and as a low refraction coefficient polymer layer polyhydroxyethylmethacrylate (PHEMA, nd=1.46) were used, and a multilayer polymer layer film was manufactured, where light with wavelengths in the range of 800 nm ~ 2000 nm, was diffracted, and it was formed as each layer thickness contained 20 combinations of high and low refractive coefficient polymer layers and by a 0.033 pitch layer thickness in the range of 0.129 microns ~ 0.327 microns space.

[0025]

Here, the polystyrene, which was a commercially available material with a molecular weight of 100,000 (manufactured by Denka Company), was prepared as a 5 % dioxane solution (viscosity : 10.0 cps), and the PHEMA was a synthesize material with a molecular weight of 100,000, and it was prepared as a 7 % methanol solution (viscosity : 12.3 cps), and they were coated. Moreover, for the PHEMA, it was synthesized by a radical polymerization as the concentration of the monomer in the methanol solution was 30 %, and 0.1 % of an initiation agent (V-65: manufactured by Shoko Junyaku Company) was used.

[0026]

For each of the coating thicknesses, the spin coating conditions of the PHEMA, are according to the shown here below table.

[0027]

| 膜厚 1 (μm) | 高屈折率材 2 (rpm) | 低屈折率率材 3 (rpm) |
|---|---|---|
| 0.129 | 2500 | 2187 |
| 0.162 | 1600 | 1400 |
| 0.195 | 780 | 973 |
| 0.228 | 816 | 714 |
| 0.261 | 624 | 546 |
| 0.294 | 492 | 430 |
| 0.327 | 400 | 350 |

1. layer thickness

When the diffraction coefficient of the obtained diffraction lattice was measured by using an optical spectrophotometer (UV-365: manufactured by Shimazu), it was understood that it maintained a homogeneous diffraction coefficient of 48 % over a range of 800 nm ~ 2000 nm.

[0028]

Practical Example 2

As the high refraction index polymer layer and as the low refraction index polymer layer, the shown here below ionized radiation curable type composition materials, were used.

[0029]

High refraction index polymer layer

urethane acrylate (PR-202:manufactured by Mitsubishi Kasei Company) ..........................................50 weight parts
2,4,5 -tribromophenolmethacrylate ..........................................150 weight parts
(manufactured by Shoko Junyaku Industries)
dipentaerithritolpentaacrylate
(Satoma-399: manufactured by Satoma Company)...............................5 weight parts

viscosity : 10 cps, refraction coefficient: 1.58

Low refraction index polymer layer

urethane acrylate (PR-202:manufactured by Mitsubishi Kasei Company) ..........................................50 weight parts

| 膜厚 1 (μm) | 高屈折率材 2 (rpm) | 低屈折率材 3 (rpm) |
|---|---|---|
| 0. 129 | 2500 | 2187 |
| 0. 162 | 1600 | 1400 |
| 0. 195 | 780 | 973 |
| 0. 228 | 816 | 714 |
| 0. 261 | 624 | 546 |
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index polymer layer and the low refraction index polymer layer are coated in order and by that they are laminated. And because of that, a laminated layer is obtained where the spaces between the layers are different and by that it is possible to easily manufacture a diffraction lattice with a wide range of diffraction wavelengths.

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[0027]

2,2,3,3-tetrafluoropropylacrylate ..........................................150 weight parts
(commercial product, manufactured by Daikin Kasei Company)
dipentaerithritolpentaacrylate
(Satoma-399: manufactured by Satoma Company)..............................5 weight parts

viscosity : 8 cps, refraction coefficient: 1.47

The conditions of the spin coating for each of the different layer thicknesses of the high refractive index and the low refractive index materials, are shown according to the table here below.

[0030]

| 膜厚 1 (μm) | PSt (rpm) | PHEMA (rpm) |
|---|---|---|
| 0. 129 | 625 | 1331 |
| 0. 162 | 400 | 852 |
| 0. 195 | 278 | 592 |
| 0. 228 | 204 | 435 |
| 0. 261 | 156 | 332 |
| 0. 294 | 123 | 262 |
| 0. 327 | 100 | 213 |

1. layer thickness, 2. high refractive index material, 3. low refractive index material

Regarding each layer, after the spin coating, it was irradiated with 5 Mrad by using an electron beam (device manufactured by ESI company) and by that it was cured and a polymer layer was obtained. Regarding each of the layer thicknesses, the high refractive index layer and the low refractive index layer were mutually combined in 10 groups and laminated in order, and by that the diffraction lattice was manufactured.

[0031]

When the diffraction coefficient of the obtained diffraction lattice was measured by using an optical spectrophotometer (UV-365: manufactured by Shimazu), it was understood that it maintained a homogeneous diffraction coefficient of 52 % over a range of 800 nm ~ 2000 nm.

[0032]

**[Results from the invention]**

As it is clear from the above described, according to the manufacturing method for the preparation of a diffraction lattice according to the present invention, it is manufactured as a layer that is formed from 2 or more polymers with different refraction indices so that the refraction indices are repeated in the order :relatively high - low. And the laminated film is obtained as the high refraction index polymer layers and the low refractive index polymer layers are coated in that order. Because of the fact that it is a laminated layer film where the thickness of the space between the layers, is varied, it is possible to have a range of the refracted wavelengths.

[0033]

In more detail, for example, it is possible to diffract at wavelengths in the range of 800 nm ~ 2000 nm. In this case, it becomes a good heat rays reflecting layer, which is permeable to the visible light, but reflects the heat rays. Such a layer reflecting the heat rays can be used in automobile and hosing construction windows, and by that it is possible to reduce the increase of the temperature inside cars and houses.

[0034]

Also, besides that, there are also other applications like color filters, used in liquid crystal displays where a light with specific wavelength from the visible light region, is reflected, film cutting off the ultra-violet rays etc..

**[Simple explanation of the figures]**

[Figure 1]
It is a figure representing a sectional view of the laminated film of one detailed example of a diffraction lattice, manufactured according to the present invention.

[Figure 2]
It is a figure representing the diffraction properties of the diffraction lattice according to Figure 1.

**[Explanation of the signs]**

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[0032]

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The conditions of the spin coating for each of the different layer thicknesses of the high refractive index and the low refractive index materials, are shown according to the table here below.

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| 0. 195 | 278 | 592 |
| 0. 228 | 204 | 435 |
| 0. 261 | 156 | 332 |
| 0. 294 | 123 | 262 |
| 0. 327 | 100 | 213 |

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Regarding each layer, after the spin coating, it was irradiated with 5 Mrad by using an electron beam (device manufactured by ESI company) and by that it was cured and a polymer layer was obtained. Regarding each of the layer thicknesses, the high refractive index layer and the low refractive index layer were mutually combined in 10 groups and laminated in order, and by that the diffraction lattice was manufactured.

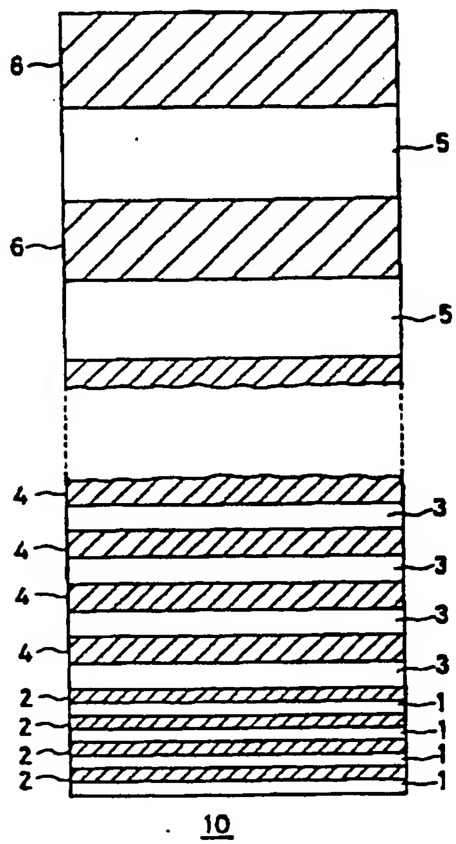
[0031]

1............................high refraction index polymer layer with a layer thickness of 0.13 microns (nd = 1.59)
2............................low refraction index polymer layer with a layer thickness of 0.13 microns (nd = 1.41)
3............................high refraction index polymer layer with a layer thickness of 0.14 microns (nd = 1.59)
4............................low refraction index polymer layer with a layer thickness of 0.14 microns (nd = 1.41)
5............................high refraction index polymer layer with a layer thickness of 0.67 microns (nd = 1.59)
6............................low refraction index polymer layer with a layer thickness of 0.67 microns (nd = 1.41)
10..........................diffraction lattice (layer thickness 70 microns)

In Figure 2:
on the vertical axis - diffraction coefficient
on the horizontal axis - diffraction wavelength

**Patent Assignee: Dainippon Printing Company**

【図1】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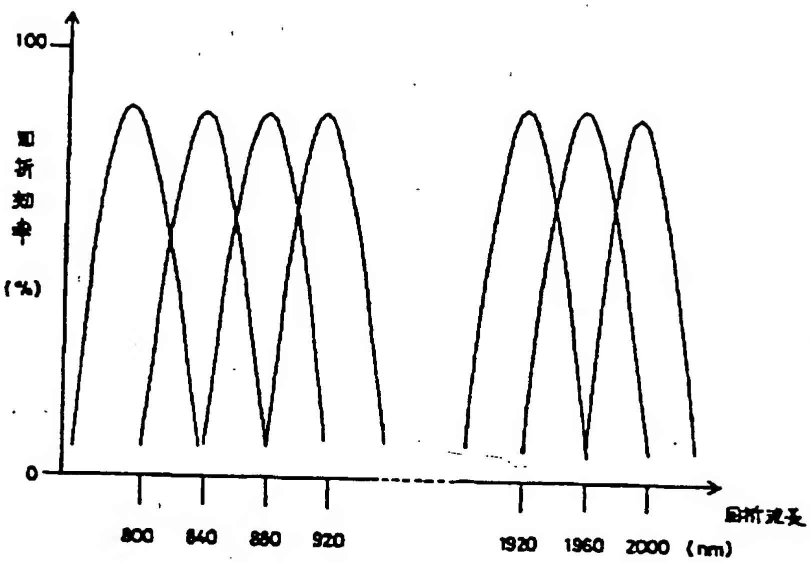
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(%)
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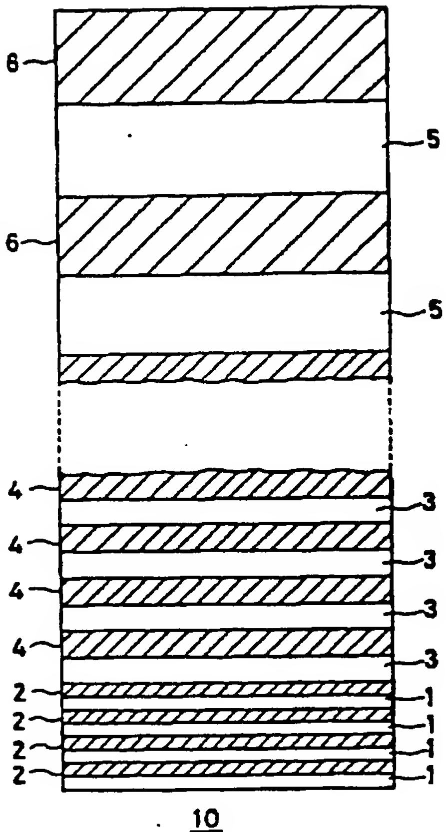
800
840
880
920
1920
1960
2000
(nm)
回折波長

【図1】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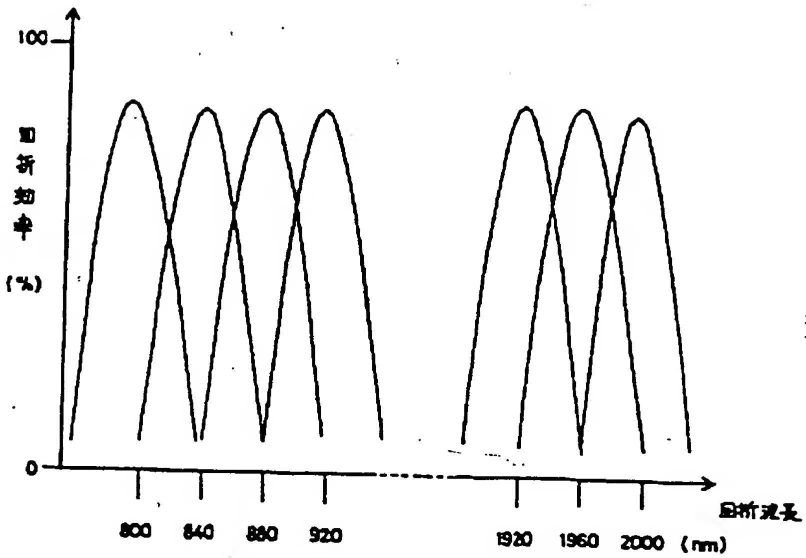
10

【図2】


100
0
回折効率
(%)
800
840
880
920
1920
1960
2000
(nm)
回折波長

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2............................low refraction index polymer layer with a layer thickness of 0.13 microns (nd = 1.41)
3............................high refraction index polymer layer with a layer thickness of 0.14 microns (nd = 1.59)
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5............................high refraction index polymer layer with a layer thickness of 0.67 microns (nd = 1.59)
6............................low refraction index polymer layer with a layer thickness of 0.67 microns (nd = 1.41)
10..........................diffraction lattice (layer thickness 70 microns)

In Figure 2:
on the vertical axis - diffraction coefficient
on the horizontal axis - diffraction wavelength

**Patent Assignee: Dainippon Printing Company**

*Translated by Albena Blagev (6-7946)*

*10/14/95*